

Chemical Speciation of PM_{2.5} in Urban and Rural Areas

Abstract

Data from the Interagency Monitoring of PROtected Visual Environment (IMPROVE) and the Speciation Trends Network (STN) are used to analyze the chemical composition of PM_{2.5} and to explore issues associated with interpretation of their measurements. The data from the largely rural IMPROVE network and urban STN are used to examine spatial patterns and to develop estimates of the local urban excess over the regional background concentrations. This work will give some insights into which of the chemical constituents are driving urban excess of PM_{2.5} mass in different regions of the United States.

Introduction

With the promulgation of the new Particulate Matter National Ambient Air Quality Standards (PM_{2.5} NAAQS), all future designated nonattainment areas and surrounding regions may need to reduce emission of fine particles and their precursors to permit those areas to attain the NAAQS. Efficient air quality management requires knowing which sources contribute to the problem and how much. Determining PM_{2.5} source contributions is complicated due to the fact that often half or more of the PM_{2.5} mass is composed of secondarily formed species,¹ hiding their point of origin. In addition, PM_{2.5} has a lifetime on the order of several days,² enabling

sources up to 1,500 miles away to affect a source region.

This work examines a simple subset of the source apportionment problem by providing evidence for local and regional source contributions and first-order approximations of their respective contributions to the following major urban areas: Fresno, CA, Missoula, MT, Salt Lake City, UT, Tulsa, OK, St. Louis, MO, Birmingham, AL, Indianapolis, IN, Atlanta, GA, Cleveland, OH, Charlotte, NC, Richmond, VA, Baltimore, MD, and New York, NY. This is accomplished by computing urban excess concentrations—by comparing annual concentrations of PM_{2.5} mass and its most abundant chemical species at the urban monitors with nearby rural monitors. In the process of arriving at the urban excess numbers, several graphics are used to show the chemical species that make up PM_{2.5} mass across the United States.

Data Sources

Ambient monitoring data from the PM_{2.5} chemical Speciation Trends Network (STN) and the Interagency Monitoring of PROtected Visual Environmental (IMPROVE) aerosol monitoring network were the main sources of data used to assess the urban and rural PM_{2.5} species concentrations across the United States.

The PM_{2.5} STN was established by regulation³ and is a companion network to the mass-based Federal Reference Method (FRM) network implemented in support of the PM_{2.5}

NAAQS. EPA established the STN network to provide nationally consistent speciated PM_{2.5} data for the assessment of trends at representative sites in urban areas across the country. As part of a routine monitoring program, the STN quantifies mass concentrations and PM_{2.5} constituents, including numerous trace elements, ions (sulfate, nitrate, sodium, potassium, ammonium), elemental carbon, and organic carbon. The STN began operation in late 1999, and there are currently a total of 54 STN sites.

In 1987 the IMPROVE aerosol monitoring network was established between Federal and State agencies to provide information for determining the types of pollutants and sources primarily responsible for visibility impairment within federally designated Class I areas.⁴ Ambient aerosol mass concentrations have been measured under the IMPROVE program to characterize the visibility conditions in these Class I areas since 1988. Over the past few years, the IMPROVE network has expanded from its original 20 monitoring sites to 110 sites in 2002. In addition, there are currently over 50 supplemental sites in regionally representative rural areas that deploy the exact same aerosol monitoring protocol. As with the STN, the IMPROVE network also quantifies mass concentrations and PM_{2.5} constituents.

Both the STN and IMPROVE programs employ a 1-in-3-day sampling protocol.

Data Work-Up

The time period chosen for this analysis is the 1-year period from March 2001 to February 2002. Any references to an annual average will refer to these 12 months. Out of the possible 54 STN sites, 35 had “complete” annual data. Similarly, 98 IMPROVE sites had “complete” annual data for this time period. Complete data, for the purposes of this analysis, refers to 50% or more of the “relevant” species observations being present for the four quarters that make up the 12 months from March 2001 to February 2002. To be consistent with previous EPA characterizations⁵ of the composition of ambient $PM_{2.5}$, the following “relevant” chemical species that make up $PM_{2.5}$ mass are considered in this analysis. The relevant species for the STN are nitrate, sulfate, organic carbon, elemental carbon, ammonium, and the trace elements that go into the “crustal” calculation: aluminum, silicon, calcium, iron, and titanium. Similarly, for IMPROVE, the relevant species are nitrate, sulfate, organic carbon, elemental carbon, and the same five trace elements that go into the “crustal” calculation. Because both networks employ a 1-in-3-day sampling protocol, the 50% completeness criterion amounts to there being 15 or more observations per quarter. No further requirement was imposed for matching days among sites or between networks. Quarters for the 12 months analyzed are defined in Table 1.

Figures 1 and 2 show the 35 STN and 98 IMPROVE locations that had complete data, as defined by the completeness criterion defined above, for the time period analyzed.

Table 1. Quarter Definitions

Quarter	Months Used in Analysis
1	January 2002, February 2002, March 2001
2	April 2001, May 2001, June 2001
3	July 2001, August 2001, September 2001
4	October 2001, November 2001, December 2001

Figure 1. 35 STN locations.

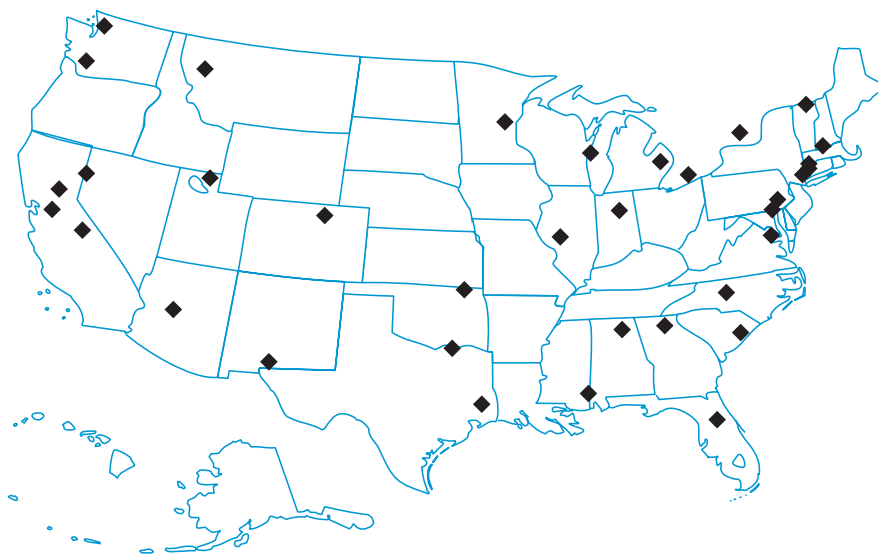
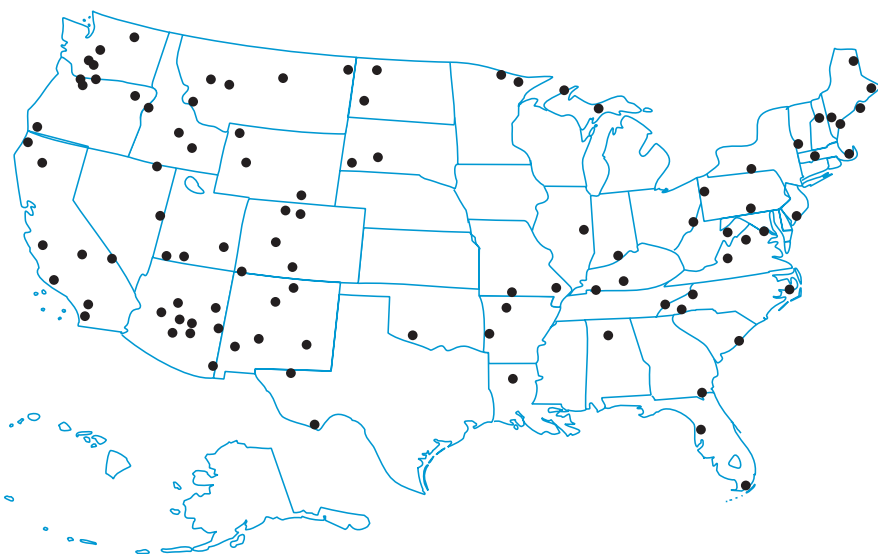


Figure 2. 98 IMPROVE locations.



Data Handling Protocols

Even though the STN and IMPROVE networks use similar sampling and analytical methods, there are differences in the species they measure and the operational protocols they employ. To put aerosol composition data derived from both these networks on an as-similar-as-possible basis, the following data handling protocols were employed:

- **Ammonium:** Although directly measured ammonium as performed by STN is important in characterizing the composition of PM_{2.5}, network-wide IMPROVE measurements are currently lacking in this area. Ammonium concentrations are thus estimated for IMPROVE (and for comparison purposes, for STN as well) from sulfate (SO₄) and nitrate measurements, assuming (1) all sulfates are ammonium sulfate (NH₄SO₄), and (2) all nitrates are ammonium nitrate. For now, the inter-network measure based on assumed ammonium sulfate and assumed ammonium nitrate compounds is more comparable and will therefore be used to define urban excess. These "estimated" ammonium concentrations are the values shown on all graphics that compare rural and urban ammonium concentrations.
- **Sulfate:** The IMPROVE program estimates sulfate concentrations as three times the sulfur concentration, whereas with the STN program, sulfate concentrations are used as measured. In this analysis, the sulfate ion measurement is used from both networks to represent sulfates.
- **Carbon:** Carbon is monitored somewhat differently by the IMPROVE and STN programs.

The variances in their analytical and sampling procedures effectively result in two different operational definitions of organic and elemental carbon.^{5,6} For this reason, organic (OC) and elemental carbon (EC) are not analyzed separately. Instead, total carbonaceous mass (TCM) is estimated as: $TCM = k * OC + EC$ for both programs. Here k is the factor for converting measured organic carbon to organic carbon mass (to account for hydrogen, oxygen, etc.). Historically, EPA and IMPROVE programs have used $k=1.4$ to convert from carbon to carbon mass. Most recent findings by Turpin et al.⁷ suggest that a higher factor to convert carbon to carbon mass may be needed in both urban and rural areas. In this work, both $k=1.4$ and $k=1.8$ are used to represent TCM. In some cases, TCM ($k=1.8$) is used to show total carbonaceous mass, whereas in other cases, comparisons are made between use of $k=1.8$ and $k=1.4$.⁷

The OC measurements reported by STN are blank-corrected data using network-wide estimates.⁵ This is consistent with the approach used

by the IMPROVE program.⁶ The OC values reported by the IMPROVE program are automatically blank-corrected using an appropriate blank correction factor.⁶ Table 2 lists the OC blank correction factors used for each of the speciation samplers that are in the STN network (also shown for comparison purposes is the IMPROVE blank correction factor). It should be noted that only organic carbon concentrations for the STN are blank-corrected (none of the other STN chemical constituents nor the total gravimetric mass is blank-corrected in this analysis).

Urban PM_{2.5} Excess

Local and regional contributions to the urban centers were estimated by computing the differences between the concentrations of the annual average urban and nearby rural monitoring data. These estimates are thus a first approximation of local and regional contributions of PM_{2.5} mass and its chemical constituents to the urban areas investigated. Although strong regional similarity exists for each of the chemical species on a large spatial scale, there are still local gradients that exist in the rural concentration domain. See, for example, Figures 3

Table 2. Organic Carbon (OC) Blank Correction Factors

Speciation Sampler	24-h Sample Volume, m ³	OC Blank Correction Factor (µg/m ³)
MetOne SASS	9.6	1.40
Anderson RASS	10.4	1.28
R&P 2300	14.4	0.93
URG MASS	16.7	0.56
IMPROVE	32.8	0.4

Soil: The soil component of PM_{2.5} ("crustal" material) was computed using the following formula, which is the same as that employed by the IMPROVE program⁸:

$$PM_{2.5} \text{ Fine Soil} = \text{"Crustal"} = 2.2[Al] + 2.49 [Si] + 1.63 [Ca] + 2.42 [Fe] + 1.94[Ti].$$

through 5, which show spatially averaged concentrations of carbonaceous mass, sulfates, and nitrate for the March 2001–February 2002 time period (together with the annual mean concentrations at each IMPROVE monitoring location). Thus, the location of a rural site (for eventual pairing to an urban site to determine urban increments) may influence the amount of urban excess seen for the specific chemical constituents of $PM_{2.5}$. One way to remove this effect and standardize the choice of rural background concentrations is to use spatial interpolation to determine average concentrations for any particular urban location. Although doing this for all sites is beyond the scope of this paper, spatial averaging for rural concentrations was applied, albeit in a simple manner, at two urban locations. At the St. Louis, MO, urban site, three nearby IMPROVE sites were used to determine an inverse-distance-weighted annually averaged rural concentration for each of the species. Similarly at the Atlanta, GA, urban site, two nearby IMPROVE sites were used to determine an average annual rural concentration for each of the species. See the discussion in the next section and Table 3 for more information on the choice of pairing of specific urban/rural sites. In general, this approach assumes that the $PM_{2.5}$ at the rural sites is generally representative of the upwind regional concentrations and is not significantly influenced by nearby emissions and that the regional sources (including upwind urban areas) have the same impact on the rural monitors and the particular urban monitors.

Figure 3. Spatial averaging of rural sulfate concentrations.

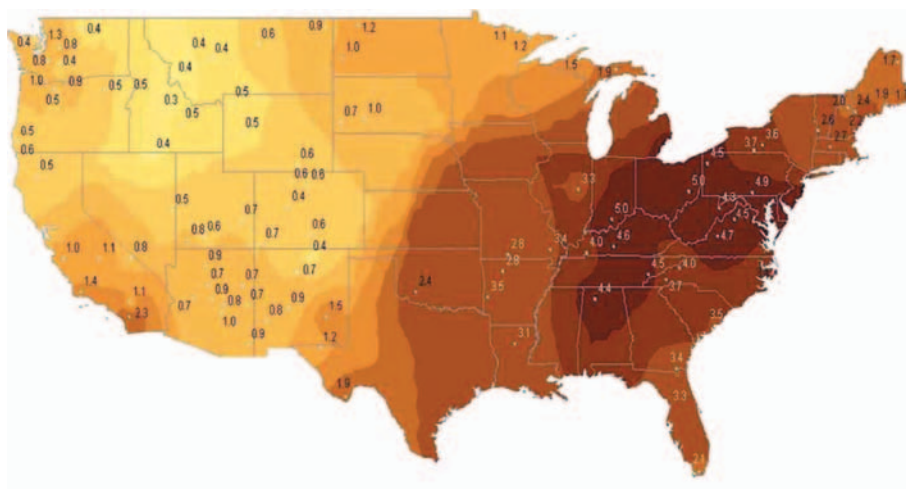


Figure 4. Spatial averaging of rural nitrate concentrations.

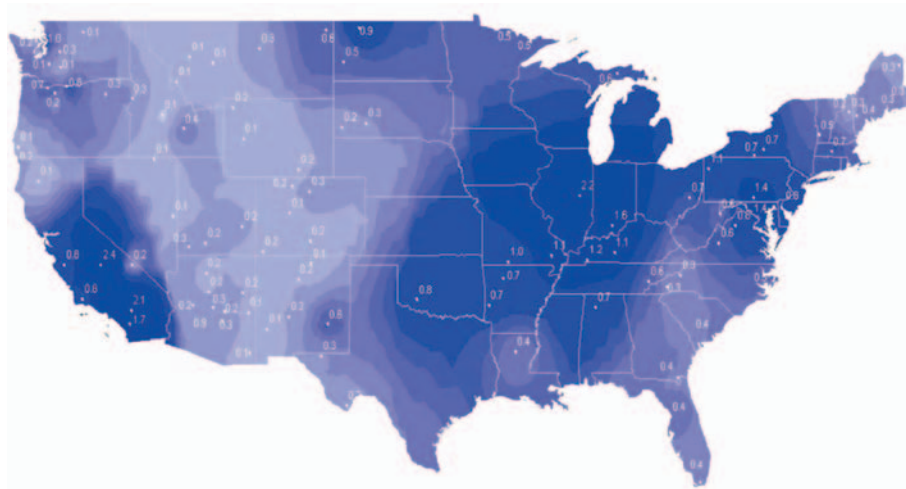
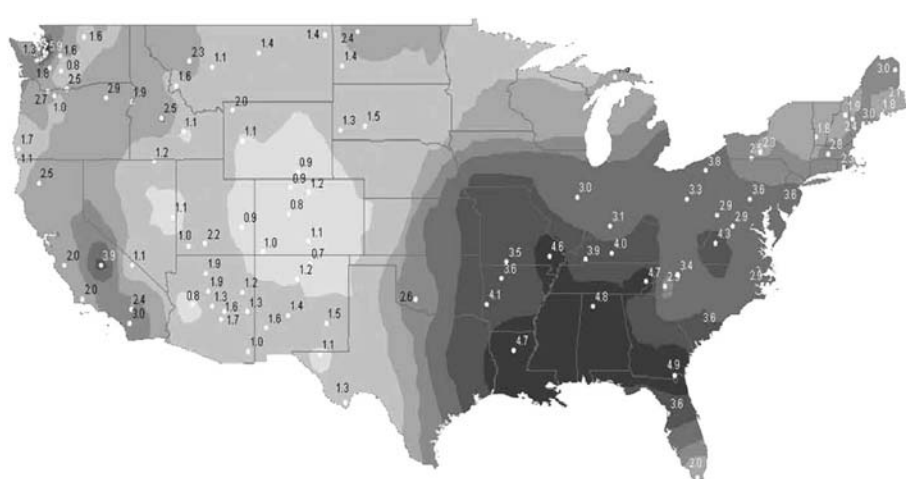


Figure 5. Spatial averaging of rural TCM ($k=1,8$) concentrations.



Choice of Urban and Rural Sites

Figure 6 summarizes the urban and rural locations chosen for this analysis. There are five urban sites (Bronx, NY, Baltimore, MD, Richmond, VA, Charlotte, NC, and Atlanta, GA) in the Northeast and Mid-Atlantic States, five urban sites stretching from north to south in the mid portion of the United States (Cleveland, OH, Indianapolis, IN, St. Louis, MO, Tulsa, OK, and Birmingham, AL), and three urban sites in the West (Fresno, CA, Salt Lake City, UT, and Missoula, MT). These were chosen due to their data being complete for the year in question as well as their ease in matching up with nearby IMPROVE rural (discussed further below) sites for the urban excess study. Except for Tulsa, they were also selected to represent States with reported $PM_{2.5}$ mass concentrations greater than $15 \mu g/m^3$, which is the level of the annual $PM_{2.5}$ NAAQS. IMPROVE sites with complete data were chosen for assumed

representativeness of upwind background concentrations. In the case of matching the urban Atlanta and St. Louis sites to nearby rural sites, a single available rural site with complete data was not judged to be sufficiently representative of the requisite

requirement, and therefore a multiple site approach (as explained above) was employed.

Table 3 summarizes all the STN and IMPROVE sites for their elevation and separation distances. For the analyses of urban excess, all

Figure 6. Thirteen urban/rural site pairings.

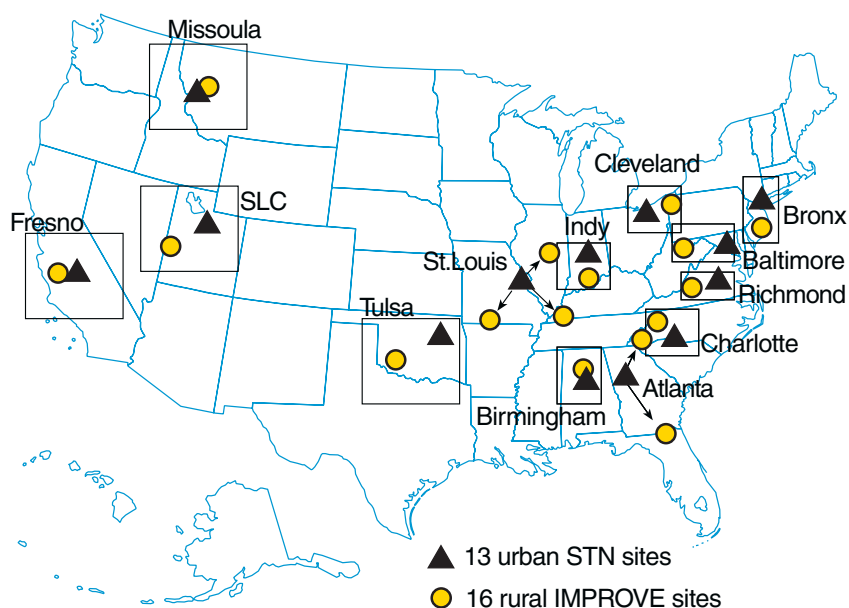


Table 3. STN and IMPROVE Site Particulars

Urban Location/Site	Elevation (m)	Rural Location/Site	Elevation (m)	Distance Apart (km)
Fresno, CA	96	Pinnacles National Monument, CA	317	28
Missoula, MT	975	Monture, MT	1,293	72
Salt Lake City, UT	1,306	Great Basin National Park, NV	2,068	277
Tulsa, OK	198	Wichita Mountains, OK	487	298
St. Louis, MO	0	Cadiz, KY	188	296
		Hercules-Glades, MO	423	322
		Bondville, IL	211	220
Birmingham, AL	174	Sipsy Wilderness, AL	279	100
Indianapolis, IN	235	Livonia, IN	298	142
Atlanta, GA	308	Okefenokee National Wildlife Refuge, GA	49	324
		Shining Rock Wilderness, NC	1,621	236
Cleveland, OH	206	M.K. Goddard, PA	383	129
Charlotte, NC	232	Linville Gorge, NC	986	132
Richmond, VA	59	James River Face, VA	300	179
Baltimore, MD	5	Dolly Sods/Otter Creek Wilderness, WV	1,158	256
Bronx, NY	0	Brigantine National Wildlife Refuge, NJ	9	165

urban/rural pairings were elevation-adjusted to account for the effect of 24-h average sample volume density on aerosol concentration. Both IMPROVE- and STN-reported data represent local conditions. This elevation adjustment was done in two steps: (1) all the concentrations from the IMPROVE sites were adjusted to sea-level conditions, and (2) all these sea-level-adjusted concentrations were adjusted once again to the elevation corresponding to the matched urban site. Except for the St. Louis and Atlanta STN monitors and their pairing with rural IMPROVE monitors, all other STN sites were matched one-on-one with the rural monitors listed in Table 3. In the case of St. Louis, the three IMPROVE monitors shown in Table 3 as matched sites were inverse-distance weighted, and the urban Atlanta site was compared to the averaged concentration(s) derived from the two IMPROVE sites shown in Table 3.

Elevation Effects on $PM_{2.5}$ Concentrations

As mentioned previously, all the IMPROVE data were adjusted for elevation (based on temperature and barometric pressure correction factors) twice: once to adjust to sea level and then again, as necessary, to adjust to the elevation of the matched urban site. Basically, this elevation adjustment is a small technical correction to make the "urban excess" calculation more meaningful. Other than at the Dolly Sods/Baltimore rural/urban pairing of sites, however, the urban/rural elevation differences were small, and these adjustments are very minor as can be seen in Figures 7 through 11, which show the effects of elevation adjustments for all the chemical species of interest at the 13 urban/rural paired combinations.

Figure 7. Effect of evaluation on rural sulfate concentrations.

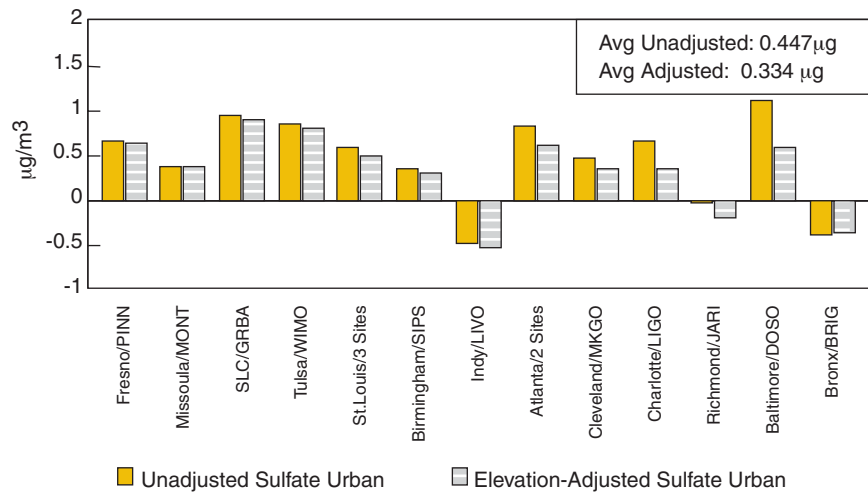


Figure 8. Effect of evaluation on rural ammonium concentration.

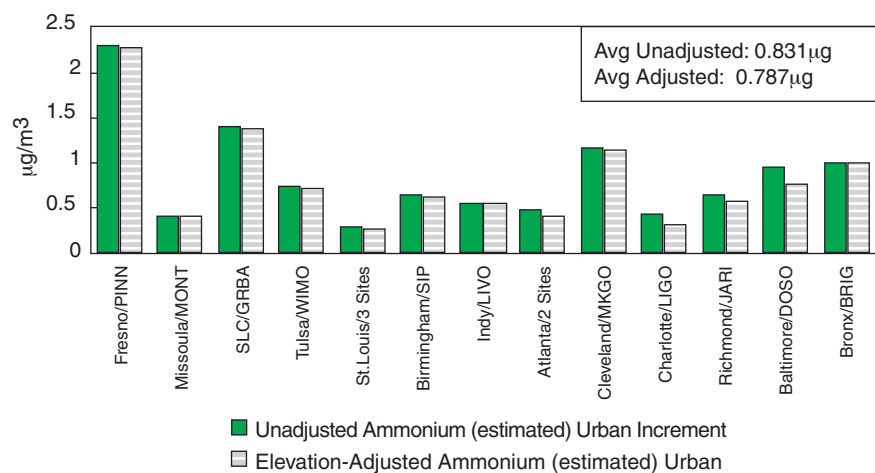
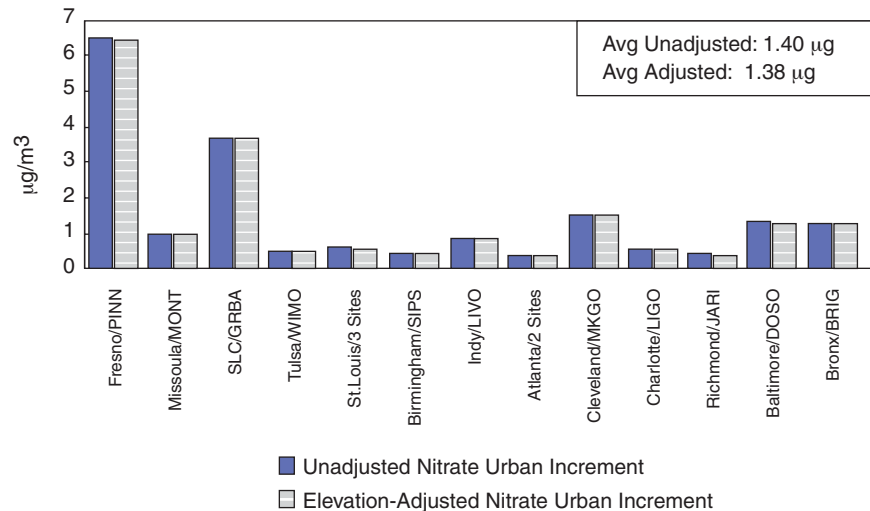


Figure 9. Effect of evaluation on rural nitrate concentration.



Urban Increments of $PM_{2.5}$ Mass and the Chemical Species

Urban sites were paired with matched rural sites as listed in Table 3, and the annual average concentrations were calculated for both the urban sites and the companion rural site(s). All rural values reflect elevation-adjusted values. These averaged rural concentrations were subtracted from the appropriate urban concentrations to arrive at the urban increments of mass and increments of the individual chemical species.

Shown first in Figure 12 is the comparison of urban concentrations to estimated regional background for total measured gravimetric mass. The difference is the "urban increment." The height of each bar represents the annually averaged urban gravimetric mass. Overlaying the nearby rural gravimetric mass on top of the urban mass levels shows how much of the total mass can be attributed to rural vs. urban sources. It can be seen that Fresno, Cleveland, and Birmingham are the urban sites in this analysis with the largest urban $PM_{2.5}$ mass during the time period investigated. The largest urban increment in $PM_{2.5}$ mass is seen to be at the Fresno, CA, site, with an average excess of about $18 \mu\text{g}/\text{m}^3$. The smallest urban increment for mass is seen to be at the St. Louis site, which shows an average urban excess of about $5 \mu\text{g}/\text{m}^3$ total $PM_{2.5}$ mass. Although this result suggests that there are more local sources influencing urban $PM_{2.5}$ mass at the Fresno, CA, location than at the St. Louis, MO, location, the selected rural sites in the eastern United States may be more reflective of background concentrations. The Fresno site may be influenced by other $PM_{2.5}$ sources throughout the

Figure 10. Effect of elevation on rural TCM ($k=1.8$) concentrations.

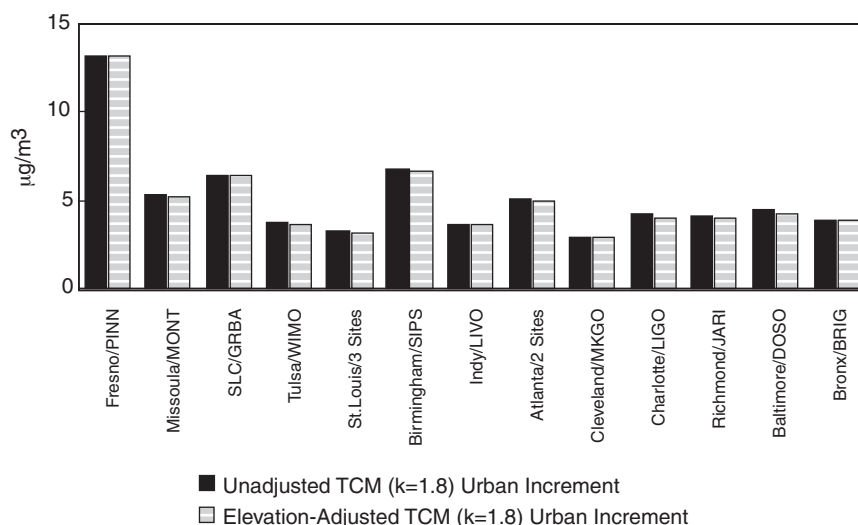


Figure 11. Effect of elevation on rural crustal concentrations.

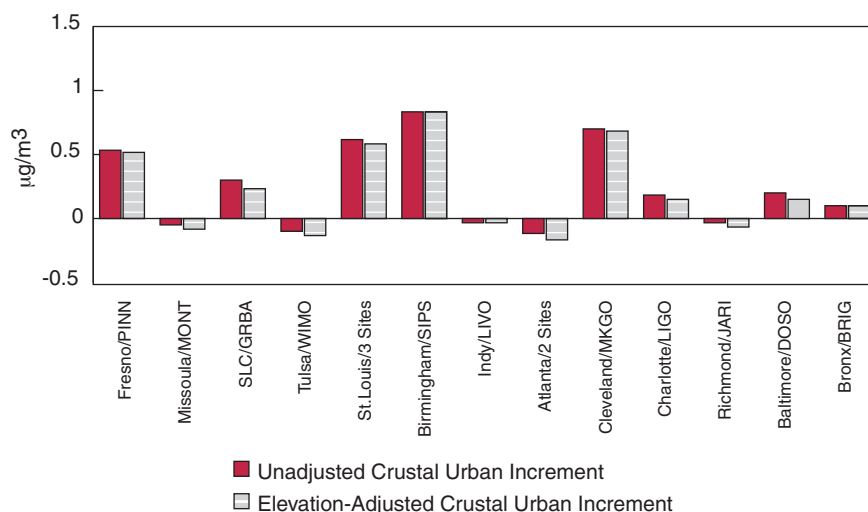
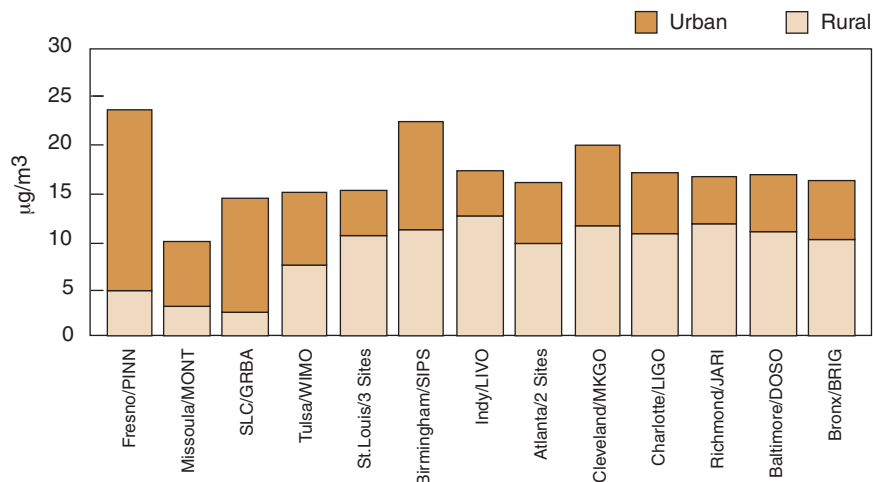


Figure 12. Urban excess for total $PM_{2.5}$ gravimetric mass.



San Joaquin Valley. In general, the total excess mass ranges from 4 to 16 $\mu\text{g}/\text{m}^3$, with the West generally showing more mass urban excess than the East. On average, the urban excess in $\text{PM}_{2.5}$ mass for the investigated 13 site combinations is seen to be about 8 $\mu\text{g}/\text{m}^3$.

Figures 13 through 16 show a comparison of urban concentrations with estimated regional background for four example sites (urban sites: Fresno, CA, St. Louis, MO, New York, NY, and Charlotte, NC—see Table 3 for the matched rural sites for these urban locations) out of the total 13 urban/rural pairings investigated. The height of each bar represents the average urban concentration by species. Overlaying the nearby rural concentrations by chemical component on the urban chemical component concentrations, the example stacked bar charts (Figures 13-16) show that the estimated regional background represents varying proportions of the total urban concentrations by component and location. Specifically, TCM and nitrates dominate Fresno particulate aerosol, whereas carbon and sulfates are the highest among the example eastern sites. In terms of urban excess, all four of these examples show TCM and nitrate concentrations to be the major components. Urban increments of TCM are seen to range from 13 $\mu\text{g}/\text{m}^3$ at the Fresno, CA, location to about 3 to 4 $\mu\text{g}/\text{m}^3$ at the other three locations. Similarly, nitrate urban excess is seen to be 6.5 $\mu\text{g}/\text{m}^3$ at the Fresno, CA, location and is in the 0.5 to 1.3 $\mu\text{g}/\text{m}^3$ range at the other sites studied. As stated earlier, the Fresno values are probably reflective of contributions from the San Joaquin Valley.

Another interesting way to look at urban excess at the 13 selected urban/rural pairs is by examining

Figure 13. Urban excess at Fresno, CA.

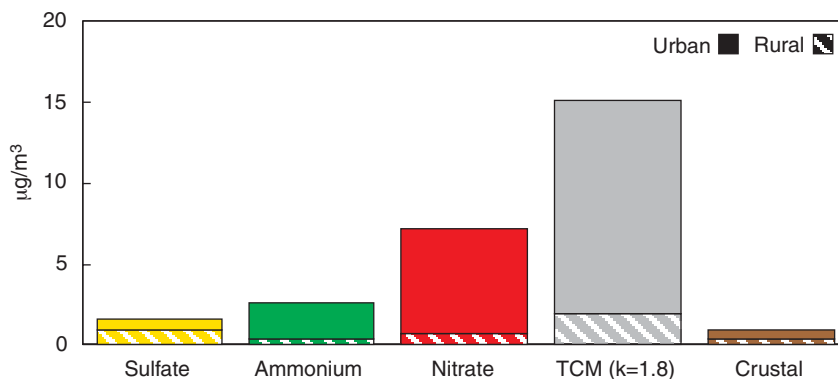


Figure 14. Urban excess at Charlotte, NC.

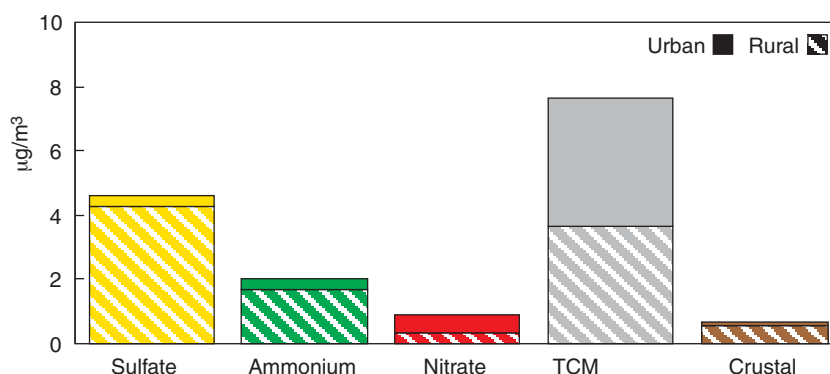


Figure 15. Urban excess at St. Louis, MO.

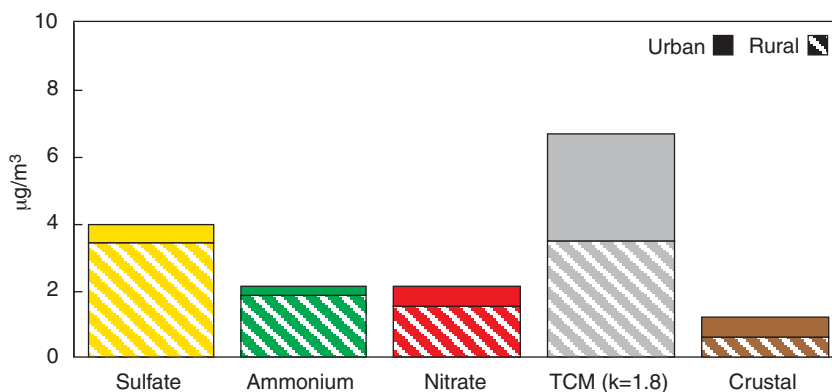
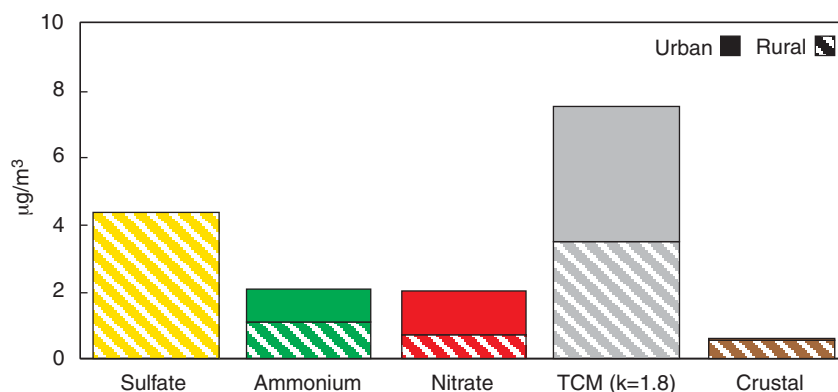


Figure 16. Urban excess at New York City, NY.

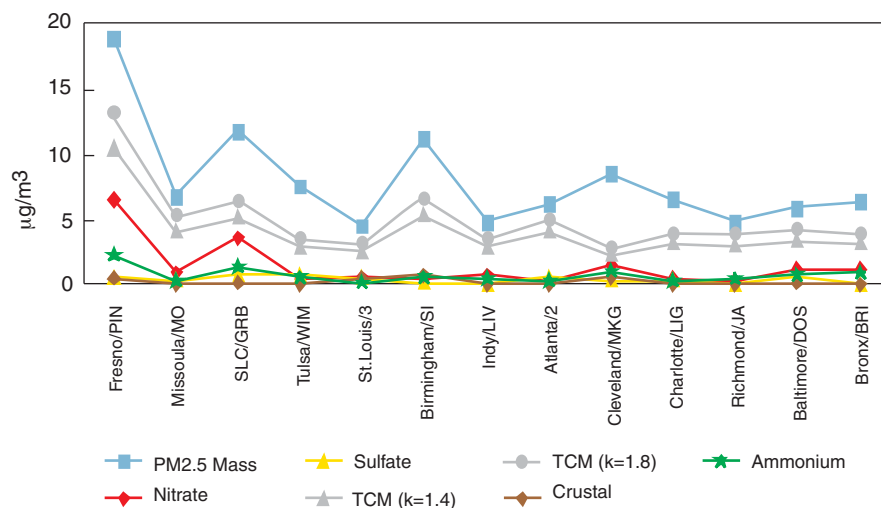


the urban increment of gravimetric mass as it compares to the urban increments of each of the chemical species that drive that mass. This is shown in Figure 17. The top line in Figure 17 depicts the total $PM_{2.5}$ mass urban excess for these 13 urban/rural site combination pairs. The urban mass is derived from the STN speciation samplers. The urban sites are arranged to reflect a west-to-east trend as you go from left to right on the graph. At all locations, total carbonaceous mass is seen to be the major contributor to $PM_{2.5}$ mass, and, at the western sites, nitrates also play a role in determining the total $PM_{2.5}$ mass increments for the time period investigated. The average excess urban mass seen in the eastern sites is 5 to 8 $\mu\text{g}/\text{m}^3$ with carbon contributing between 3 and 5 $\mu\text{g}/\text{m}^3$ to the mass increment. The exception to this average is the Birmingham, AL, urban site. This site is paired with the Sipsy Wilderness rural site (~100 km away) to estimate urban excess. Birmingham shows a mass increment of about 12 $\mu\text{g}/\text{m}^3$, with carbon contributing about 5.0 to 6.5 $\mu\text{g}/\text{m}^3$ to the total mass increment. Birmingham probably has local (urban) emissions sources that are contributing to the $PM_{2.5}$ mass. To understand why the mass is so much higher in the urban Birmingham area compared with the other eastern sites studied, more work is needed to investigate how these sources differ from emissions sources in the other eastern locations.

National Map of Urban Excess

The estimated urban excess concentrations are displayed in the national map shown in Figure 18 for the selected 13 urban/rural combinations. Table 4 presents these same findings through summary statistics.

Figure 17. Comparison of mass urban increment to chemical species.



Those urban excess numbers that were less than zero were set equal to zero in Table 4 (the “minimum” values for sulfate and crustal concentrations in the “East” and “Overall” columns). However, the actual numbers, both positive and negative, were used to compute average concentrations (of urban excess concentrations).

The significant points and important caveats are as follows:

- The estimate for urban excess sulfate is invariably very small in the eastern United States, which is consistent with the notion that most sulfates are transported from regional sources of SO_2 . This small estimated urban excess in the East ($0.0\text{--}0.5 \mu\text{g}/\text{m}^3$) is attributed at least in part to sulfur emissions associated with fuel combustion from stationary and mobile sources.
- Nitrates are seen to be in excess in the more northern and western locations, showing a larger local contribution than sulfates or any other species except carbon. This is assumed to reflect local nitrogen sources (e.g., mobile), nitric acid from NO_x/VOC reactions, and preferential winter-time nitrate formation compared to sulfates. However, more work is needed to assess the comparability of nitrate measurements and monitoring methods between networks. To that end, a major study is planned next year by the IMPROVE program. This was initiated, in part, because there is concern that the IMPROVE protocol may produce relatively lower concentrations of nitrates, so some of the reported difference may be measurement related.
- Carbonaceous mass is shown to have a substantial urban excess (2.9 to $13.2 \mu\text{g}/\text{m}^3$ when $k=1.8$). It is clearly the largest among all reported chemical components in this “urban excess” analysis. It appears to be attributed to local emissions, with mobile sources as a possible major contributor.
- Some locations also show a sizeable urban excess of “crustal material.” The estimation procedure used in the IMPROVE protocol includes the measurement of iron and other trace elements.

Therefore, this difference also reflects oxidized particulate metals, some of which may be attributed to road dust or industrial sources in urban areas.

Conclusions

In this work, the local and regional source contributions of PM_{2.5} to urban areas were investigated at 13 urban locations in the United

States. This was accomplished by matching urban sites to nearby rural sites and then comparing the appropriate concentrations of chemical constituents and mass. Although

Figure 18. National map depicting urban excess by component for 13 example areas.

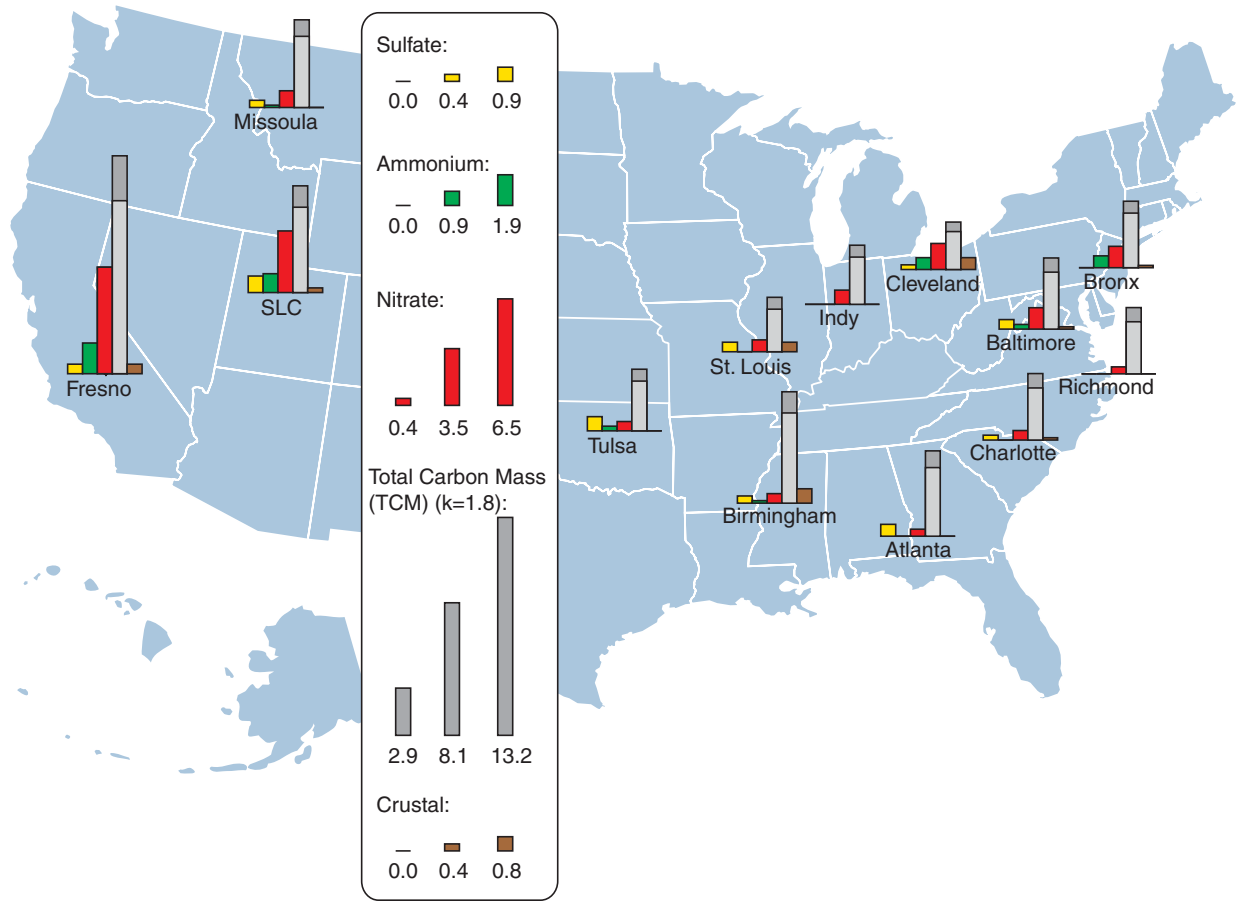


Table 4. Minimum, Maximum, and Average Urban Excess in µg/m³ for 13 STN/IMPROVE Combinations

	West (3 sites)			East (10 sites)			Overall (13 sites)		
Chemical Species	Min	Max	Average	Min	Max	Average	Min	Max	Average
Sulfate	0.4	0.9	0.6	0	0.8	0.3	0	0.9	0.3
Estimated Ammonium	0.4	2.3	1.4	0.3	1.1	0.6	0.3	2.3	0.8
Nitrate	1.0	6.5	3.7	0.4	1.5	0.8	0.4	6.5	1.5
Total Carbonaceous Mass (k=1.4)	4.2	10.5	6.6	2.4	5.4	3.3	2.4	10.5	4.1
Total Carbonaceous Mass (k=1.8)	5.3	13.2	8.3	2.9	6.7	4.2	2.9	13.2	5.1
“Crustal”	-0.1	0.5	0.2	0	0.8	0.2	0	0.8	0.2

there is uncertainty in the measured mass and in other measurement protocols, it is clear that carbonaceous mass is prevalent everywhere (average of $5.1 \mu\text{g}/\text{m}^3$ with $k=1.8$) and is the major component of urban excess at all the sites studied. In the western sites, the TCM (based on $k=1.4$) urban excess varies from 4.5 to $10.5 \mu\text{g}/\text{m}^3$, whereas in the eastern sites, TCM urban excess is in the range of 2 to $5.4 \mu\text{g}/\text{m}^3$. TCM, based on $k=1.8$, varies from a range of 5.3 to $13.2 \mu\text{g}/\text{m}^3$ in the West and to a range of 2.9 to $6.7 \mu\text{g}/\text{m}^3$ in the East. Similarly, nitrates are prevalent in the urban excess estimates for the North and West (2 to $6 \mu\text{g}/\text{m}^3$). Consistent with the theory that most sulfates are transported from regional sources of SO_2 , the urban excess of this chemical component is invariably very small in the eastern United States. These results may be viewed as a first step in differentiating between regional and local sources that contribute to $\text{PM}_{2.5}$ mass. More work is needed in the areas of estimating regional background associated with specific urban areas using spatial analysis, identifying specific emission sources with the estimated urban excesses using source apportionment techniques, more refined data analysis that includes meteorological variables, and examination of the data on finer time resolution to get to the next and more refined level of urban excess concentrations. These will be the subjects of future papers in this area.

Disclaimer

The views and opinions expressed in this paper are solely those of the authors and do not necessarily reflect those of the U.S. Environmental Protection Agency.

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